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CHEMICAL EXCHANGE REACTION

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CZECHOSLOVAKIA

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THE CONCENTRATION OF ISOTOPE  $N^{15}$  BY A  
CHEMICAL EXCHANGE REACTION

[This is a translation of an article written  
by A. Zeman\* and V. Cermak in Chemické listy,  
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Description of the construction and operation of a column for the concentration of  $N^{15}$  by a chemical exchange reaction between ammonia and ammonium ions. The  $N^{15}$  content was increased to 11.4 percent by using a packing of glass cloth in a single-column apparatus.

Chemical exchange reactions are one of the very efficient means of enriching isotopes. The method is used in particular for the concentration of  $C^{13}$ ,  $N^{15}$ , and  $S^{34}$ ; they can be especially applied for research by the labeled-atom method. Substances enriched with stable isotopes are particularly needed since the development of mass spectrometry permitting a precise measurement of the natural and artificially changed ratio of isotopes.

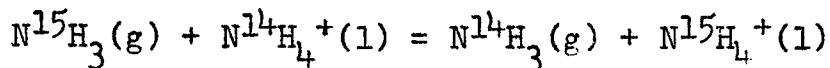
In connection with the construction of a mass spectrometer at the Institute of Physical Chemistry of the Czechoslovak Academy of Sciences (Ústav fyzikální chemie CSAV / Československá akademie věd /) it was decided in 1952 to build an apparatus for the concentration of the  $N^{15}$  isotope by the chemical exchange reaction between gaseous ammonia and ammonium ions, in a solution according to Urey<sup>†</sup>, in order to obtain ammonium salt enriched to a certain degree with  $N^{15}$ , to gain experience in the construction and operation of exchange columns, and to find a more efficient packing for such columns.\*\*

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\*\*This work was not published until now because the results obtained in 1952, and checked then by emission molecular spectra of enriched nitrogen in the region 3159 to 3165 Å (See 5) were finally established by the mass spectrometer analysis only last year.

The principles of the isotope-concentration method using a chemical exchange reaction were developed by Urey and Greiff<sup>6</sup>, who showed theoretically that the isotope compounds of the lighter elements differ only slightly in their chemical behavior, who calculated the equilibrium constants of a series of exchange reactions in the gaseous phase and, with a view to the possibility of practical use, proposed that the exchange reactions be carried out between two different phases in an arrangement which would permit a manifold repetition of the exchange.

The exchange reaction between gaseous and aqueous  $\text{NH}_4\text{NO}_3$  solution for the enrichment of  $\text{N}^{15}$  according to Urey used



whose equilibrium constant is

$$K = \frac{\boxed{\text{N}^{14}\text{H}_3} \boxed{\text{N}^{15}\text{H}_4^+}}{\boxed{\text{N}^{15}\text{H}_3} \boxed{\text{N}^{14}\text{H}_4^+}} \quad 1$$

and has the value of 1.023 (see 1,4) for a sixty-percent aqueous solution of  $\text{NH}_4\text{NO}_3$ . Gaseous ammonia of a natural composition (0.365 at. %  $\text{N}^{15}$ ) is thus in an isotope equilibrium with ammonium ions containing 0.374 at. %  $\text{N}^{15}$ . The shift in concentration is very slight.

The exchange reaction is, therefore, performed in counter-current columns with a suitable packing (Fig. 1). A  $\text{NH}_4\text{NO}_3$  solution with the natural content of  $\text{N}^{15}$  is fed to the top of the column. After passing through it all ammonia is liberated by adding alkali in the stripping column and it is drawn counter currently through the exchange column, where it comes into active contact with the  $\text{NH}_4\text{NO}_3$  solution which trickles down the packing. If, at the beginning, a solution with a natural  $\text{N}^{15}$  content flows through the exchange column, ammonia with the same  $\text{N}^{15}$  content is liberated in the stripping column. A contact of the two phases at the bottom of the exchange column, however, causes the solution to become isotopically enriched and the gas to be depleted. Ammonia with an equilibrium concentration of  $\text{N}^{15}$  rises to the top of the exchange column, but the enriched solution from the bottom of the column renders ammonia with an increased  $\text{N}^{15}$  content in the stripping column; this ammonia again passes into the solution together with an additional amount of  $\text{N}^{15}$  until it is

depleted again to the equilibrium concentration. Unless the enriched product ( $\text{NH}_4\text{NO}_3$ ) is removed from the bottom of the column, the  $\text{N}^{15}$  is accumulated gradually in the column and a concentration gradient of  $\text{N}^{15}$  is set up in the column increasing downward. After attaining a steady state the volume of  $\text{N}^{15}$  flowing through an arbitrary cross section of the column in both directions would be the same and a solution of  $\text{NH}_4\text{NO}_3$  with the maximum enrichment of  $\text{N}^{15}$  would flow from the bottom of the column into the stripping column. If the  $\text{N}^{15}$  concentration in the product is not to fall, only that volume of enriched  $\text{NH}_4\text{NO}_3$  (or  $\text{NH}_3$ ) can be removed daily which accumulates in the column during one day, that is

$$q = \frac{Ax_0 - By}{x_0 - x_0}$$

where  $q$  is the volume of enriched  $\text{NH}_4\text{NO}_3$  in mol/24 hours that can be removed,  $A$  is the volume of normal  $\text{NH}_4\text{NO}_3$  in mol/24 hours introduced on the top plate,  $B$  is the volume of  $\text{NH}_3$  in mol/24 hours withdrawn from the exchange column,  $x_0$  is the mole fraction of  $\text{N}^{15}$  in the normal  $\text{NH}_4\text{NO}_3$ ,  $x_k$  is the mole fraction of  $\text{N}^{15}$  in the enriched  $\text{NH}_4\text{NO}_3$ , and  $y$  is the mole fraction of  $\text{N}^{15}$  in the  $\text{NH}_3$  withdrawn.<sup>4, 8</sup>

The enrichment factor of the column is expressed as in the distillations columns:

$$Z = \left( \frac{\text{N}^{15}}{\text{N}} \right)_1 / \left( \frac{\text{N}^{15}}{\text{N}} \right)_2 = K^p$$

where the numerator and denominator express the ratio of the concentration of the heavy nitrogen in the liquid phase at the bottom (1) and top (2) of the column,  $Z$  is the over-all enrichment factor,  $K$  is the equilibrium constant of the exchange reaction, and  $p$  is the number of the theoretical plates<sup>9</sup>.

The attainment of a marked enrichment requires a large number of theoretical plates and if this were to be attained in a single exchange column it would have to be very high (tens of meters). A very long time would then be required for reaching the state at which it would be possible to remove the enriched production from the bottom of the column, since equilibrium in the column is reached only very slowly as a result of only a very slight deviation of the equilibrium constant from unity, and as a result of a hold-up. Usually, therefore, cascades of

two to three enriching sections are applied.<sup>(2,4,8,9)</sup> Thode and Urey<sup>4</sup> obtained in this way a product with 72.8 at. %  $N^{15}$ , and recently Spindel and Taylor<sup>10</sup> produced nitric acid with 99.5 at. %  $N^{15}$  through the exchange reaction between  $NO$  and  $HNO_3$ .

In this study the concentration process was made only in a single-column apparatus.

### Experimental Party

The enrichment column was built on the basis of test. The test column, analogous to the second section of Clusius and Beske's apparatus,<sup>8</sup> is shown in Figure 1.

The test exchange column was 11.8 meters long, with a 12 millimeter inner diameter, and consisted of three parts. Four millimeter porcelain Berl saddles were applied as packing. The stripping column - one meter long - was filled with eight millimeter long Rasching porcelain rings and had a 40 millimeter inner diameter. Both columns were made of G 20 glass. The feed of the sixty-percent solution of  $NH_4NO_3$ , partially saturated with ammonia, to the top of the exchange column, the transfer from the bottom of the individual parts of the column to the top of the succeeding part, the feed of the 14-percent solution of  $NaOH$ , and the removal of the waste (alkaline solution of  $NaNO_3$ ) were performed by  $P_1$ - $P_4$  pumps. The pumps had a tested design and were composed of a hollow aluminum cylinder in which turned a rotor with two or three rollers on its periphery.<sup>(11,14)</sup> Rubber tubes with a two-millimeter inner diameter were placed in the gap between the inner lining of the cylinder and the rollers (the tubes were lubricated with castor oil); the contents of the tubes moved in the direction of the rotor's rotation due to the squeezing action of the rollers. The pumps were mounted on a common axis. The pumping speed was 0.75 ml/minute. The pressure in the apparatus was maintained at 80 millimeter Hg by an automatic device consisting of a regulating manometer and an electric circuit controlling an electromagnet which closed the access to a water vacuum pump as necessary. The apparatus worked under conditions of a total reflux of  $N^{15}$  and worked for ten days without interruption.

The final column was 8.3 meters long and was composed of three sections; the last was 1.5 meters shorter and its lower part was directly connected to the mixing vessel

to which the solution flowed under gravity. This arrangement reduced the volume of the solution retained in the connecting tubing. For the same reason the inner diameter of the connecting tubing between the sections of the column was reduced from the original three to one millimeter. The exchange column was filled with hollow cylinders with a two-millimeter diameter and a four-millimeter length, formed by rolling a tube from glass cloth impregnated with paraffin.\*\*\* After filling the column paraffin was extracted by means of benzene and chloroform.

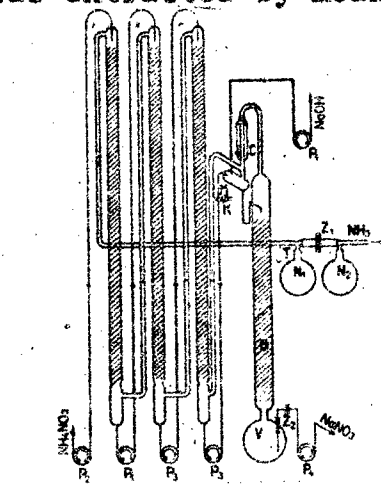


Figure 1.

#### Diagram of the Enrichment Equipment

I, II, III exchange columns; B stripping column; V boiling flask;  $P_1$ - $P_4$  pumps; C cooler; M mixing vessels;  $Z_1, Z_2$  electromagnetic valves;  $N_1, N_2$  tanks for damping pressure fluctuation; k cock for removing enriched  $NH_3$ ; T mercury regulation manometer.

Ammonia was liberated imperfectly in the stripping column of the first experimental installation, and part of it was taken away from the column in the waste. This reduced substantially the efficiency of the  $N^{15}$  concentration, and the stripping column was, therefore, lengthened to two meters in the final installation; it was fitted with an electrically heated jacket which limited the heat loss from the column and prevented its flooding.

\*\*\*The packing was supplied by the Technological Department of the Institute of Chemistry of the Czechoslovak Academy of Sciences (Technologicke oddeleni Chemického ustavu CSAV).

The enrichment installation worked 27 days with 23 days allocated for concentration and four days for production. Its operation was practically uninterrupted, except for the third day, when the apparatus had to be shut down for a short period because of an accidental plugging of the feed of  $\text{NH}_4\text{NO}_3$  to the mixing vessel. The wall of the boiling flask (made of Duran glass) had become so thin by the end of the 27th day due to the action of the caustic that the apparatus had to be shut down. A total of 17 kilograms of  $\text{NH}_4\text{NO}_3$  were consumed.

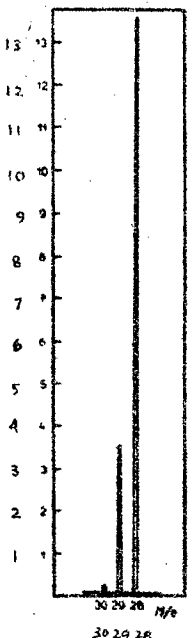


Figure 2  
Mass Spectrum of Enriched Nitrogen  
With 11.4 at. %  $\text{N}^{15}$

Current at  $M/e=28$  corresponds to the  $\text{N}^{14}\text{N}^{14+}$  ions;  
 $M/e=29$  to  $\text{N}^{14}\text{N}^{15+}$  ions; and  $M/e=30$  to  $\text{N}^{15}\text{N}^{15+}$  ions.  
The current is given in relative units.

The following defects were found during the work of the enrichment installation:

1. Part of the  $\text{NH}_4\text{NO}_3$  solution retained in the packing of the original test column at times flowed into the lower collecting vessel, interrupting the concentration gradient inside the column. The flow was caused by channels in places where the packing was not sufficiently and uni-

Table I

Comparison of the Operational Data and Results  
of the Enrichment Equipment

Author (stage) See 4 (3rd)	Length of Column (m) 7.8	Inner Diameter of the Column (cm) 1	Pumping Speed (ml/min) 0.85	Packing 5 mm Glass Spiral	Z 11.5	State Practically steady state	Height Equi- valent of the Theoretical Plate (cm) 7.3
See 8 (2nd)	11.8	1.2	1.1	4 mm Berl Saddles	10.3	After 16 Days	11.4
See 3 (3rd)	9.4	1	0.91	2 by 2 millimeter cylinders from a 2 millimeter wire spiral from stain- less steel	12.8	Practically Steady state	7.8
This work	8.3	1.2	0.75	2 by 4 millimeter cylinders from Glass cloth	35.1	After 27 days	5.3



formly piled, and by the relatively large dimensions of the packing in comparison with the diameters of the column. This defect was eliminated in the final column by careful filling and the use of a smaller-size packing.

2. In places where the packing was too much compressed the column sometimes became flooded over a length of about five centimeters and the normal compression gradient was raised (about 15 millimeters). This defect was eliminated by a slight heating of the flooded section from outside.

3. The current determination of ammonia in the waste by Nessler's reagent proved in several instances that ammonia was not boiled out perfectly, and it was therefore necessary to regulate carefully the current in the heating sections of the stripping column.

4. The porcelain packing of the stripping column was partially dissolved by the hot caustic, and a sediment accumulated in the boiling flask causing the plugging of the pump tubing. It was therefore necessary to remove the tubing from the pump several times, and to remove the waste by an auxiliary water vacuum pump. The vacuum pump was, therefore, exchanged and cleaned with hydrochloric acid.

### Results and Conclusion

Analysis of the  $N^{15}$  content in the enriched  $NH_4NO_3$  by the mass spectrometer of the Institute of Physical Chemistry of the Czechoslovak Academy of Sciences proved that after 19 days of uninterrupted operation the  $N^{15}$  content rose from 0.365 at. % to 8.3 at. %, and after nine more days (at the end of the 27th day) to 11.4 %. This maximum value corresponds to an overall enrichment factor  $Z = 35.1$ , to a number of theoretical plates  $p = 156$ , and to a length of the heights equivalent of the theoretical plate of 5.3 centimeters. A comparison of our results with the data of other authors is shown in Table I. The mass spectrum of nitrogen with 11.4%  $N^{15}$  is shown in Figure 2.

The results proved that the packing of glass cloths is more efficient than other packings which are being applied.

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